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(56) References:
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(54) [Title of the Invention] Base Film for Flexible Printed Wiring Boards

(57) [Claims]

[Claim 1] A base film for flexible printed wiring boards made from a thermoplastic polyester with a melting point of 280°C or higher.

[Claim 2] The base film for flexible printed wiring boards of Claim 1 characterized by the fact that the thermoplastic polyester is composed mainly of a 1,4-cyclohexanedimethanol component and a terephthalic acid component.

[Detailed Description of the Invention]

[Field of Industrial Utilization]

The present invention relates to a base film for flexible printed wiring boards that is made from a specific thermoplastic polyester. More specifically, the present invention relates to a base film to be used for flexible printed wiring boards that has solder heat resistance.

[Prior Art and Problems]

Flexible printed wiring boards have been becoming increasingly important in the electronics field in recent years because of their characteristics such as lightness of weight, flexibility, and mass producibility, and the quantities produced have also continued to increase. As is well known, flexible printed wiring boards are manufactured by means of bonding a copper foil to a base film using an adhesive, and a copper circuit is subsequently formed using a lithographic technique. Biaxially oriented polyethylene terephthalate film, polyimide film, and the like have conventionally been employed as base films. Large quantities of polyester film are used as base films because of its excellent mechanical strength, chemical resistance, electrical insulating property, and low cost. However, solder is used to connect the circuits in printed wiring boards, and the use of solder is also strongly desired in the field of flexible printed wiring boards. The original resin in base films made from polyethylene terephthalate has a melting point of 255°C, and therefore completely melts from the temperature of the solder usually used (about 260°C). It consequently cannot be used for such purposes, and the circuits are instead connected by means of techniques such as caulking. In contrast to this, films made from polyimide resin are base films having solder heat resistance. Polyimide films have good chemical resistance as well as very high heat resistance. They do not melt in 260°C solder baths, or even in 280°C solder baths, and also undergo very few dimensional changes. Large quantities, therefore, are currently used. However, polyimide film has the major drawbacks discussed below. Specifically, polyimide resin is highly hygroscopic. Therefore, when the manufactured wiring boards pass through the solder bath after having been stored in a warehouse or the like, bubbles sometimes develop on the film board surface due to the rapid release of the water contained in the film. This

serves to lower the product yield. The films are also very expensive, and are currently ten or more times as costly as the polyethylene terephthalate discussed above. Thus, the flexible printed wiring boards have excellent characteristics, but are used only in sophisticated electronic instruments and the like, and further progress has been met with difficulty. Films made of polyether sulfone resin, polysulfone resin, polyallylate resin, and the like have been proposed to resolve the respective drawbacks of polyethylene terephthalate films and polyimide films as described in the foregoing. Nonetheless, such films are all formed from amorphous polymers, and therefore have major drawbacks such as poor chemical resistance, and a tendency to dissolve or crack when exposed to chemicals used for lithography or etching copper foil. In addition, they are not necessarily stable under soldering at 260°C, and undergo large dimensional changes. They are therefore inadequate for use as precision circuit boards.

[Means Used to Solve the Above-Mentioned Problems]

With the foregoing drawbacks in view, the present inventors conducted in-depth studies intended to obtain an inexpensive base film having solder heat resistance and very little hygroscopicity that would not be damaged as a result of chemicals during the manufacture of flexible printed wiring boards. As a result, they arrived at the present invention by discovering that the aforementioned problems could be completely resolved by means of using a film made from a thermoplastic polyester with a melting point of 280°C or higher as the flexible printed wiring board. Specifically, the main point of the present invention is a base film for a flexible printed wiring board composed of a thermoplastic polyester with a melting point of 280°C or higher.

The present invention will be explained in detail below. The melting point in the present invention is the temperature of the apex of the endothermal peak that corresponds to the melting of crystals in DSC (differential scanning calorimetry). Since the crystals of a polyester with such a characteristic do not melt at 260°C, and the polyester remains completely solid, the film maintains a stable film shape without melting, even when immersed in a 260°C solder bath. Such a polyester film can be selected arbitrarily as long as it has a melting point of 280°C, and of preferably 290°C or higher. However, polyesters with such a high melting point generally have a high temperature at which they are moldable, and this temperature sometimes overlaps the temperature at which the ester bonds decompose. Therefore, a resin with a relatively large difference between the molding temperature and decomposition temperature is used as a

preferred thermoplastic polyester. A specific example is a polyester resin made from a 1,4-cyclohexanedimethanol component and a terephthalic acid component (abbreviated hereinafter as "PCT resin"). Small quantities of other diol components and dicarboxylic acid components may be copolymerized in the present invention as long as their melting points are not lower than 280°C. Inorganic fillers; commonly used fillers such as plasticizers; small amounts of other polymers; and the like may also be added to the polyester resin.

An example in which the base film of the present invention is manufactured will be described next. The film of the present invention is either stretched or unstretched, and preferably has a degree of crystallization of 20% or more. During molding, the film is preferably formed by means of using the following two processing techniques to attain the present object. One is a method for manufacturing an unstretched crystallized film. The other is a method for manufacturing a biaxially stretched crystallized film. An unstretched crystallized film can be obtained by means of first forming an unstretched film with the help of T-die casting, then passing the film between heated multi-stage rolls to heat set and crystallize it. Alternatively, the film can also be obtained as a result of being continuously passed through a heating zone instead of between multi-stage rolls, while being held at both ends. An unstretched crystallized film can also be obtained as a result of heating the T-die to a temperature equal to or higher than the glass transition temperature of the resin during casting. The film is preferably crystallized to a sufficient degree in order to minimize dimensional changes when immersed in the solder bath. A biaxially stretched crystallized film can be obtained by means of a two-stage biaxial stretching technique using a tenter, as is used for ordinary polyethylene terephthalate film. An alternative method involves using a tubular simultaneous biaxial stretching technique, as is used for nylon film and the like. A temperature that is equal to or higher than the glass transition temperature of the resin is preferably selected as the stretching temperature. The stretched film is also preferably orientated and crystallized to a sufficient extent by means of adequate heat setting. Either an unstretched crystallized film or a biaxially stretched crystallized film obtained with the help of such methods can be used appropriately as a base film for flexible printed wiring boards. A biaxially stretched crystallized film sometimes undergoes slight shrinkage, but will still be solder heat resistant, have good transparency, and have excellent mechanical strength. The production of spherulites causes the transparency of unstretched crystallized film to be slightly inferior to that of a biaxially stretched film, and the mechanical strength also to be slightly inferior;

however, very few dimensional changes occur even when the film is passed through solder at 260°C, and its characteristics are equivalent to those of polyimide film.

In addition to the characteristics discussed above, the base film of the present invention is made of polyester resin, thus absorbing very little water and not bubbling or displaying other problems when immersed in a solder bath. The base film also has good chemical resistance and has the advantage of not being damaged as a result of the chemicals used during production of the flexible wiring board.

[Working Examples]

The present invention is explained in greater detail below through working examples; however, the present invention shall not be limited to these working examples as long as the main point of the invention is retained.

Example of Resin Manufacture

19.4 kg of dimethyl terephthalate and 17.2 kg of 1,4-cyclohexanedimethanol, together with a phenol solution of Na-$HTi(OC_4H_6)_8$ as a catalyst, were introduced into an autoclave, kept at a temperature of 220-240°C in a nitrogen atmosphere, and demethanolized. The temperature was raised to 300°C and vacuum polymerization was then carried out. After normal pressure was reinstated, the contents were removed from the autoclave, yielding a PCT resin. η_{inh} of the resin was 0.75, as measured at 30°C at 1% by weight in a phenol/tetrachloroethane (50/50) container [sic]. The percentage of the *trans* form of the 1,4-cyclohexanedimethanol used in this example was 75 mol%.

The melting point of the resin was 292°C as measured with the help of DSC.

Example of Film Manufacture 1

A transparent film (50 μm thick) was produced from the PCT film obtained in the Example of Resin Manufacture by means of a T-die method using an extruder 30 mm in diameter. The results of x-ray diffraction measurement confirmed this film to be composed of an almost entirely amorphous structure (amorphous unstretched film). A crystallized film was obtained when part of this film was heated by means of being passed between multi-stage rolls heated to 200-275°C. The degree of crystallization was 35% (crystallized unstretched film), as measured with the help of a specific gravity technique (density gradient tube method).

Example of Film Manufacture 2

The amorphous unstretched film obtained as described in Example of Film Manufacture 1 was biaxially stretched in two stages at a stretching temperature of 120°C using a tenter, and crystallization was made to advance as a result of having the film passed continuously through a heat-set zone heated to 285°C. The established draw ratio at this time was 3 × 3. X-ray diffraction measurement revealed that the polymer chains in the film were oriented parallel to the film surface. The degree of crystallization of the film was approximately 40% based on the results of specific gravity measurement.

Working Example 1

A copper-clad laminated board was produced by means of laminating a copper foil (35 μm thick) to the crystallized unstretched film obtained as described in Example of Resin Manufacture 1 using a urethane-acrylic adhesive. A test circuit was formed on this laminated board as a result of etching the copper using a resist technique, resulting in a flexible wiring board. The appearance of cracks caused by means of the resist ink (Taiyo Ink Mfg. Co., Ltd; trade name: AS-400 SP; UV-curable), resist remover (2% sodium hydroxide aqueous solution), and etching solution (cupric chloride aqueous solution) was investigated, but none were observed.

Working Example 2

A solder resist (Taiyo Ink Mfg. Co., Ltd.; trade name: FOC-800GK) was applied to the flexible wiring board produced as described in Working Example 1, and the assembly was then passed continuously through a solder bath kept at 260°C. In addition, a punched circuit board was immersed in the solder bath for 30 seconds. Absolutely no changes could be found in the appearance or dimensions in either case. The crystallized unstretched film obtained as described in Example of Resin Manufacture 1 was also immersed as a separate item in the solder bath for 30 seconds in the same way, but no dimensional changes were observed. When the crystallized biaxially stretched film obtained as described in Example of Resin Manufacture 2 was tested by means of an immersion in the solder bath in the same way as above, absolutely no changes could be found in its appearance, but the film shrank approximately 1%. This value is acceptable for use as a flexible printed wiring board.

Comparative Example 1

A polyethylene terephthalate film (thickness: 50 μm) with a melting point of 255°C and a polyimide film (DuPont; trade name: Capton; thickness: 50 μm) were subjected to the same solder bath immersion test used in Working Example 2. The polyimide film did not exhibit any changes in its appearance, but shrank approximately 0.7%. This value is acceptable for use as a printed substrate. On the other hand, the polyethylene terephthalate film shrank simultaneously when immersed and completely melted.

Working Example 3

The copper-clad laminated boards produced as described in Working Example 1 were subjected to the same solder bath immersion test used in Working Example 2 after having stood for 10 days in a 40°C, 90% RH environment, as a result of which no cracking or the like was observed.

Comparative Example 2

A copper-clad laminated board was produced in the same manner as described in Working Example 1, except that a polyimide film (DuPont; trade name: Capton) was used. The board was subjected to a solder bath immersion test after having stood for 10 days in a 40°C, 90% RH environment in the same manner as described in Working Example 3. As a result, cracks developed in the regions where the film and copper had been bonded.

[Effect of the Invention]

The base film for a flexible printed wiring board of the present invention, in which a specific thermoplastic polyester is employed, has solder heat resistance, very little hygroscopicity, and excellent dimensional stability. The base film is also industrially advantageous because it is inexpensive and not damaged as a result of chemicals when flexible printed wiring boards are manufactured.